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The application of graphene material in the negative electrode of lithium battery

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Abstract. With the development of science and technology, the massive consumption of traditional fossil fuels not only brings serious environmental pollution but also causes an energy crisis. As an indispensable new energy in today's world, Lithium batteries have many advantages that other types of batteries do not have, such as high energy density, long life, low self-discharge rate advantages, green and environmental protection, etc., and widely used in various fields, such as automotive, medical, aerospace and so on. However, the drawbacks such as low specific capacity and high side reaction of graphite material in traditional lithium batteries limit the application of lithium batteries. Graphene, as a two-dimensional material composed of carbon atoms in a single layer thickness, possesses the advantages of huge surface area, high strength and hardness, good electrical and thermal conductivity, flexibility, and transparency, and has great potential for application in lithium batteries. In this paper, for graphene as the anode material of lithium batteries, its effects on the performance of lithium batteries, including cycling performance, charge/discharge rate, and energy density, are discussed respectively. In addition, this paper also summarizes the latest progress on the application of graphene anode materials in lithium batteries.

1 Introduction

In the process of rapid development of the global economy and science and technology, a large amount of natural energy has been exploited and utilized by people, which has led to the phenomenon of energy crisis in the world. Therefore, the research of new energy sources is of great significance. As a new generation of clean energy, lithium batteries can not only avoid the pollution of the environment, but also facilitate people's life and work, and it is widely used in consumer electronics, electric vehicles, medical equipment, space and aerospace, energy storage systems, and other fields.

The structure of a lithium battery is mainly divided into four parts: positive electrode, negative electrode, electrolyte, and diaphragm. Among them, the negative electrode material plays an important role in lithium batteries. It is the key part of the lithium battery for storing and releasing energy. During the charging process, the anode material can absorb lithium ions, while during the discharge process, it releases lithium ions, thus realizing the conversion and storage of energy. The performance of anode materials also directly affects the first cycle efficiency, cycle life, multiplier performance, and safety performance of lithium batteries. High-quality anode materials can increase the number of cycles of the battery, and reduce energy loss while ensuring the safety of the battery in the process of use [1].

Traditional graphite materials as anode in lithium batteries usually have relatively low specific capacity, irreversible capacity loss in the first charge/discharge, insufficient multiplicity performance, sensitivity to electrolyte, poor safety, and other problems, that limit the development of lithium batteries.

For nearly 20 years, graphene has had a broad application prospect in the field of lithium batteries due to its high specific surface area, high electrical conductivity, excellent mechanical properties, structural stability, and other advantages [2]. Therefore, this paper focuses on the impact of graphene as a lithium battery anode material, which has a reference role in the study of lithium batteries.

2 Improving the cycle life of the lithium batteries

As a new type of material, graphene has unique advantages in improving the cycle life of lithium batteries. In addition to preventing lithium ion accumulation and improving battery stability and safety, graphene can also effectively increase the conductivity and transmission rate of the electrode, thereby improving the energy density and charging and discharging efficiency of the battery [3]. This means that by applying graphene to the negative electrode of a lithium battery, the service life of the battery can be significantly extended and its performance can be improved. Not only that, graphene also has good mechanical properties, which can enhance the durability and compression resistance of lithium batteries, making them more

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suitable for various harsh environmental working conditions. Moreover, the high conductivity and thermal stability of graphene also help to avoid the loss and heat generation of electrode materials in the process of charging and discharging, improving the efficiency and safety of lithium batteries. Graphene has a broad application prospect in the field of lithium batteries, which will bring great impetus and improvement space for the development of future battery technology.

As a new type of energy storage device, graphene-based pseudocapacitors have high energy density and cycle stability. Figure 1 shows the performance test results of the graphene-based pseudapacitor capacitor. It can be seen from the figure that the charge-discharge curves of the graphene-based pseudocapacity capacitor show good electrochemical performance under different current densities, showing its excellent energy storage properties. The graphene-based pseudocapacitor also shows high cycle stability and long cycle life, which makes it a new type of energy storage device with broad application prospects.

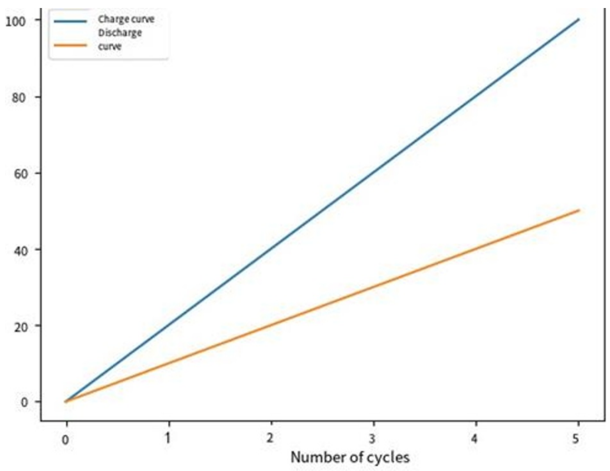

Fig. 1. Graphene-based pseudocapacitor performance.

New materials formed by the composite of graphene and carbon nanotubes: The application of carbon nanotube composite materials in the field of lithium battery negative electrodes has attracted much attention. The composite of graphene and carbon nanotube can give full play to the advantages of both and improve the performance of batteries [4]. At present, the preparation methods of graphene and carbon nanotube composites mainly include chemical vapor deposition, mechanical grinding, and solution mixing. In addition, microscopic observations have shown that After being irradiated with HCPEB, the graphite particles formed stone wells and double-vacancy defects in the process of in-situ conversion to self-supporting graphene nanosheets due to the continuous high temperature. The experimental results show that the reversible capacity of the modified 12μm natural graphite electrode is 420.4mAh/g under the condition of 0.2C, and the reversible capacity can still be maintained by 94.5% after 500 cycles of charge and discharge. Compared with unmodified graphite with a particle size of 12 μm, SEI film has higher stability and significantly improved cycling performance.

Nitrogen doping can introduce additional electrons into the graphene structure, thereby improving its electrical conductivity. In addition, doping of nitrogen atoms can also change the electronic structure of graphene, increase its interaction with lithium ions, and improve its cycle stability and capacity in lithium batteries. A common preparation method for nitrogen-doped graphene is to introduce ammonia or nitrogen gas into the graphene material, which is doped with nitrogen atoms into the graphene structure through heat treatment. Doped graphene materials generally exhibit better electrochemical properties, showing potential applications. Therefore, the application of nitrogen-doped graphene materials in the negative electrode of lithium batteries is of great significance and is expected to improve its cyclic performance [5].

3 Improving the charging and discharging rate of lithium batteries

Using graphene as a negative electrode material for lithium batteries can significantly improve the charge and discharge efficiency of the battery, mainly due to its unique physical and chemical properties. First, graphene has excellent electrical conductivity, which can significantly improve the conductivity. In lithium batteries, the conductivity of the electrode material is one of the key factors affecting the charge/discharge rate. Therefore, by introducing graphene, the performance of lithium batteries during high-current charging and discharging is effectively improved. Secondly, the two-dimensional layered structure of graphene can effectively inhibit the pulverization of the electrode material caused by volume changes. This helps maintain the stability of the electrode structure, thus ensuring that the battery can be continuously and stably charged and discharged. In addition, graphene can also improve the cycle stability of lithium batteries. During the charging and discharging process of lithium batteries, the structural stability and cycling performance of the electrode materials are critical to the overall performance of the battery. The introduction of graphene helps to reduce the performance degradation of the electrode materials during the cycling process, thus improving the cycle life of the battery.

At present, researchers have conducted in-depth discussions on the application of graphene in improving the charging and discharging rate of lithium batteries, and are constantly looking for more effective methods and technologies to improve the performance and stability of batteries. By improving the structure and properties of graphene materials, it has been applied to the negative electrode materials of lithium batteries, and certain results have been achieved [6]. In a report, Mand Khan Bakht et al mentioned that transition metal oxide particle surface-modified graphene is a new anode material for lithium batteries, which has a large specific surface area and excellent electrical conductivity [7]. The preparation methods mainly include chemical vapor deposition and chemical reduction. Chemical vapor deposition is done by heating a volatile carbon source on a metal substrate so that it is deposited on the surface to form graphene [8]. The chemical reduction principle is to reduce graphene oxide and metal oxide particles into a metal compound and graphene complex in a solution [9]. Transition metal oxide particle surface-modified graphene has high conductivity and lithium storage properties, which can effectively improve the cycle stability and energy density of lithium batteries. It is characterized by the fact that after modification, the graphene surface forms a tight bond with metal oxide particles, effectively improving the electron transport rate and the lithium-ion diffusion rate. At the same time, graphene, as a conductive scaffold and stabilizer, improves the cycle life and safety of lithium batteries. In addition, Researchers proposed that conductive polymer surface-modified graphene has excellent electrical and mechanical properties, making it an ideal choice for lithium battery anode materials. Conductive polymers can effectively improve the conduction efficiency between graphene and lithium ions, thereby improving the charge and discharge performance.

4 Improving the energy density of lithium batteries

Graphene plays a significant part in improving the energy density of lithium batteries. On the one hand, graphene has a very high specific surface area and electron mobility, which means it can effectively adsorb more lithium ions, and lithium ions migrate faster in graphene. As a result, it can significantly increase the specific capacity of the battery, which in turn improves the energy density of the battery. On the other hand, graphene has excellent electrical conductivity, which helps to reduce the internal resistance of the battery and improve the energy conversion efficiency of the battery. By optimizing the conductivity of the electrode materials, the energy density of lithium batteries can be further improved. In addition, to the flexibility and stability of graphene, graphene can maintain structural integrity and reduce the volume change of the active material during the battery charging and discharging process, thus avoiding energy loss due to structural damage.

A novel silicon-doped graphene material (SiG) was reported by Liu [10]. Their solid-state SiG was constructed by utilizing the in-situ microwave radiation doping method. This method has low cost and mass production potential. First, graphene is obtained by supercritical CO_2 exfoliation. After doping, silicon heteroatoms at the edges and surfaces of graphene provide more defects to interact with Li^+. This mechanically suppressed silicon doping enhances the specific capacity and significantly mitigates the volume expansion of silicon atoms. Compared with pristine graphene (PG) anodes, SiG anodes have higher efficiency, larger specific capacity, and faster rate performance. The experimental results show that the complex process of doping silicon heteroatoms into graphene lattice can be accomplished well by microwave irradiation, which doubles the specific capacity of pristine graphene, as shown in Figure 2. More importantly, SiG exhibits improved storage and diffusion of Li^+ after the cycle, in addition to the increase in energy density and the rise in power density, which are attributed to the Si heteroatoms dispersed on its surface and the more ordered graphene lattice.

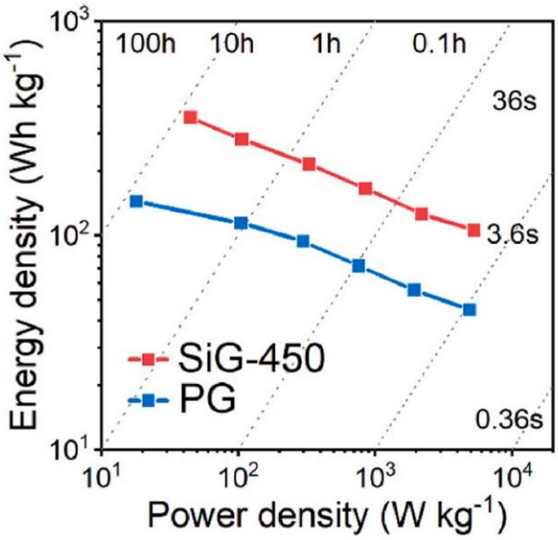

Fig. 2. Ragone plot of PG and SIG-450 [10].

In a report, Han Meisheng et al. proposed a multi-layer carbon structure strategy and successfully prepared a new composite material, called C/VGSs@Si-C, as shown in Figure 3. The carbon matrix in subnanometer C, vgs, and SI-C together constructed a three-dimensional conductive robust network, significantly increased the EC of Si (9.3×10^{-3}S m^{-1}), and inhibited the volume expansion of Si, which was characterized by a 27.5% increase in electrode thickness after more than 100 cycles. Because highly conductive vgs have a large number of exposed edges, it provides many fast channels for Li^+ directional transmission. The carbon matrix coated with VGSs@Si-C reduces the specific surface area, increases the cone density, and obtains a higher CE head and electrode compaction density. Because of these obvious advantages, C/VGSs@Si-C exhibits excellent Li^+ storage performance under industrial electrode conditions.

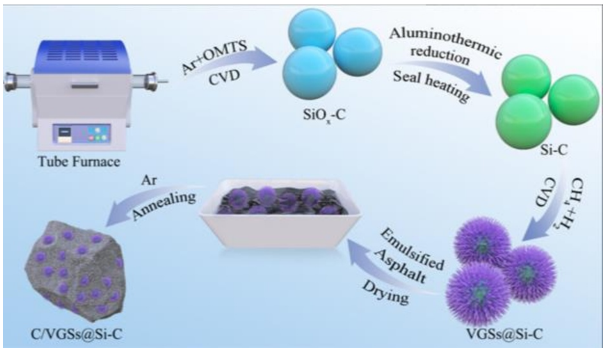

Fig. 3. Synthesis diagram of C/VGSs@Si–C [11].

In half batteries, C/VGSs@Si-C offers high capacity and high capacity retention, as shown in Figure 4. In particular, fully charged batteries have good high-speed charging capabilities with high energy density and long cycle life; For instance, after 16.5 min of charging at 3 °C, the energy density maintains about 81% of that at 1/10 °C, the capacity retention rate is near 81% at 1 °C after about 500 cycles. Therefore, the C/VGSs@Si-C anode has better practicability for fast-charge batteries and high-energy-density lithium-ion batteries. Particularly, at 0.1°C, the full battery has an energy density of 603.5, still maintaining an energy density of about 81% at 3°C [11].

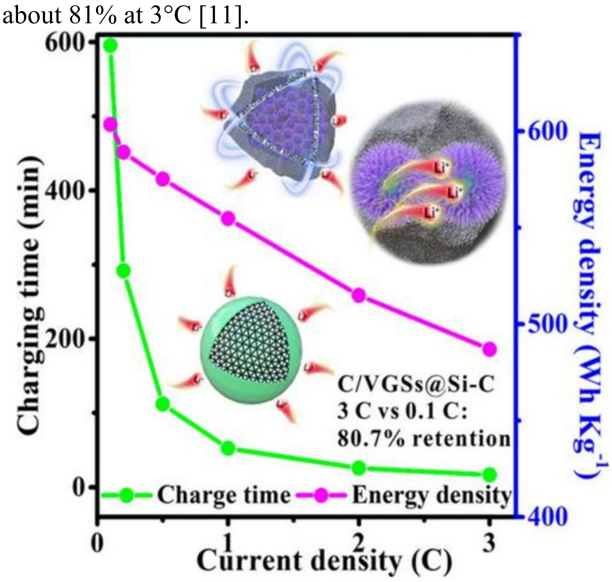

Fig. 4. Energy density curve of C/ VGSs@Si-C [11].

5 Conclusion

The high conductivity and high specific surface area of graphene make it an ideal cathode material for lithium batteries. It has high thermal conductivity, flexibility, and tensile resistance, which can enhance the heat dissipation effect, cycle life, and safety of batteries. By using high-performance materials such as graphene, the energy density of lithium batteries can be increased to achieve higher-performance battery applications.

Although graphene has many potential advantages in lithium batteries, it also has some limitations. First, the production cost of graphene is relatively high, which makes graphene far more expensive to produce than traditional anode materials such as graphite. Second, the energy storage mechanism of graphene has not been fully clarified. Its energy storage performance is not always superior to that of other materials, which may be because the energy storage mechanism of graphene is relatively complex and involves a variety of factors, such as surface structure, defects, impurities, and so on. These factors may affect the stability of graphene's performance in lithium batteries. In addition, the safety of graphene lithium batteries is also an issue of concern. Due to the excellent conductivity of graphene, once a short circuit or overheating occurs, it may lead to a rapid release of energy inside the battery, which may cause safety problems. Finally, the cycle life and energy density of graphene lithium batteries have improved, but have not yet reached the desired level. Although graphene has excellent performance in theory, its performance may not be fully utilized in practical applications due to limitations in material preparation and battery design.

People should further improve and optimize graphene preparation technology and battery design methods in the future, to reduce the cost of graphene preparation and improve the cycle life and energy density of lithium batteries. More importantly, new electrochemical systems and battery structures should also be developed to enhance the intelligence and automation of the battery management system, to effectively reduce the probability of safety problems with graphene batteries and reduce the safety hazards caused by short-circuit and overheating problems. It is believed that the deepening of the research will bring more innovative breakthroughs and development opportunities for the advancement of battery technology and the development of new energy fields.

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